

Laboratory Investigation of Transport and Treatment of Chromium in Groundwater at Liwa district, Abu Dhabi

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1.0 Introduction

Groundwater quality is a critical aspect affecting utilization of this source for certain purposes. In the UAE, utilization of groundwater for domestic purposes is well practiced. While the quality of groundwater at some locations does not permit direct utilization of this source, groundwater, in many cases, is mixed with desalinated water at certain proportion before being disinfected and then distributed to customers.

Groundwater of Liwa aquifer contains high level of Cr(VI). It is believed that this contaminant originates from natural sources, but little has been done to investigate the fate of this contaminant. Spreading of chromium to nearby aquifers may render the quality of these aquifers unsuitable for certain uses. Furthermore, groundwater in Liwa district may not be suitable for drinking purposes even when mixed with desalinated water. It was, therefore, necessary to understand the impact of different transport mechanisms including advection, dispersion, and soil interaction on the transport of Cr(VI) in groundwater at Liwa district. This is important for the success of future measures to decontaminate groundwater in Liwa area. Another objective of this study was to investigate removal of Cr(VI) using activated carbon and metal iron.

Several batch and column studies were conducted to investigate the transport of Cr in Liwa soil. Batch studies revealed that Liwa soil has low sorption capacity to Cr(VI) and higher sorption capacity to Cr(III). Sorption distribution coefficients for Cr(VI) determined from column experiments were more reliable than results obtained using batch tubes since the latter method is not sensitive to chemicals that are slightly sorbed to solids.

Miscible displacement experiments conducted using Cr(VI) on columns packed with Liwa soil suggested that differences in the initial concentration used or differences in the applied flow rates employed do not result in a significant impact on the shape of the breakthrough curve. Normalized effluent Cr(VI) concentration along with the corresponding values of the pore volume (PV) were utilized to determine the value of the hydrodynamic dispersion coefficient (D) and the retardation factor and (R) using CXTFIT_{2.0}. The model was further used to simulate Cr transport under different conditions. In conclusion, columns packed with Liwa soil have dispersivity of 0.4 cm and a retardation coefficient for Cr(VI) of about 1.5.

Reduction of Cr(VI) using iron was investigated under different pH values. Addition of iron to a solution containing Cr(VI) caused the disappearance of the chemical. It was also found that as the pH is reduced from 7 to 4, higher removal occurred with almost complete disappearance of Cr(VI) from solution at pH 4 after 2 hrs of contact time.

The rate of change of Cr(VI) and total Cr concentration with the use of granular activated carbon (GAC) at different pH values was investigated. The results of the experiments showed that the concentration of Cr(VI) decreases with time in the presence of GAC, with more disappearance from solution as the pH drops. In both the carbon and the iron experiment, the actual mechanism of Cr(VI) disappearance from solution is not clear.

2.0 Materials and Methods

2.1 Description of the study area

The Liwa Crescent is a 160-kilometer long arcuate area that demarcates the transition within central Abu Dhabi Emirate between low-relief sand dunes of the northern sand-sea region and relatively high-relief sand dunes and sabkhas on the south. Figure 3.1 shows the location of the Liwa Crescent.

The total cultivated area within the Liwa district is about 64 million m² distributed as forests, fodder farms, and palm trees and vegetable farms.

2.2 Hydrology of the Liwa aquifer

The Liwa aquifer is roughly lens-shaped, with a maximum observed thickness of about 121 m. The aquifer has a specific yield that averages 0.22 and a transmissivity of 300 m²/day. The estimated rate of decline of the water table during the years 91-93 was about 25 cm/yr. The groundwater moves in either northward or southward directions toward topographically low areas that comprise the coastal sand salt flats and the sand dune and sabkha physiographic regions, respectively.

The Liwa Crescent area can be divided into 3 primary areas with respect to recharge potential: sand dunes, interdune areas, and sabkhas. In sand dune areas, there is practically no runoff over the surface of the sand. The average grain size of dune crests is 0.17 mm. The ages of the water samples range from 10,000 to 28,000 years. Thus, water being withdrawn from aquifers underlying these areas is fossil water that recharged the aquifer during a period of wetter climatic conditions several thousands years ago.

2.3 Chromium Interaction with Liwa Sand

2.3.1 Cr(VI) rate experiments

Results of Cr(VI) rate experiments at three different S/W ratio are presented in Figure 2.1. It is clear from the figure that the sorption capacity of the sand is negligible and the slight variations observed in the concentration of Cr(VI) as compared to the initial value may be within the uncertainty of the analytical technique itself.

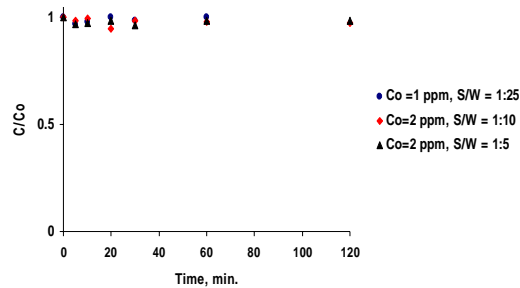


Figure 2.1 Rate of sorption of Cr(VI) by Liwa sand at different S/W ratio.

2.3.2 Cr(III) rate experiments

Figure 2.2 shows the results of Cr(III) rate experiments. Obviously, the sorption capacity of Liwa sand to Cr(III) is very high contrary to its capacity to sorb Cr(VI). Inability of Liwa soil to sorb Cr(VI) is possibly due to the fact that the source of Cr(VI) is chromate which will be repelled by the negatively charged silt fraction of the soil. However, Cr(III) adheres to these silt particles.

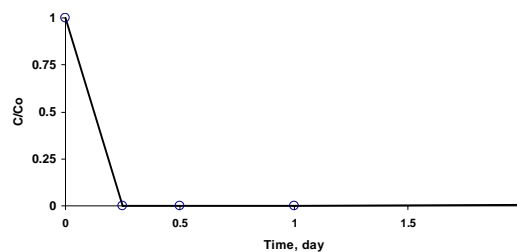


Figure 2.2 Rate of sorption of Cr(III) to Liwa sand, $C_0 = 50$ ppm, S/W = 1:40.

2.3.3 Sorption isotherm experiments

Sorption isotherm highlights the relationship between the concentration of Cr in the liquid and solid phases by finding the distribution coefficient (K_d) of the target element between the solid and the liquid phase. The results are shown in Figure 5.3. In the Figure, S_e and C_e stand for the equilibrium concentration of Cr(VI) on the soil and in the solution, respectively. The values of S_e were determined by mass balance using values for the initial and final concentration in the aqueous phase. Figure 2.3 clearly shows that Liwa soil has low capacity to sorb Cr(VI), consistent with the findings of the rate experiment.

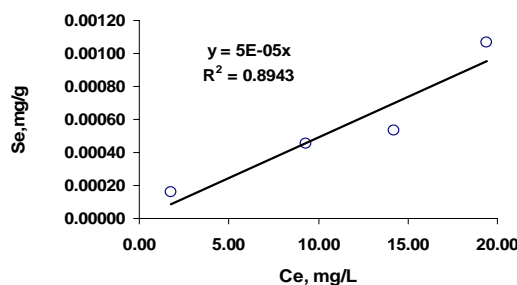


Figure 2.3 Sorption isotherm of Cr(VI) to Liwa soil at a S/W ratio of 1.5:1.

On the other hand Figure 2.4 shows that Liwa soil has higher capacity to sorb Cr(III), consistent with the findings of the rate experiment.

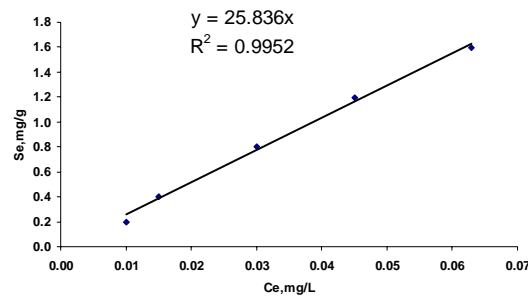


Figure 2.4 Sorption isotherm of Cr(III) to Liwa soil at a S/W ratio of 1:40.

2.3.4 Column experiments

Results of three miscible displacement experiments conducted using Cr(VI) on columns packed with Liwa soil are shown in Figure 2.5. The experiments differ in the initial concentration injected or the applied flow rate.

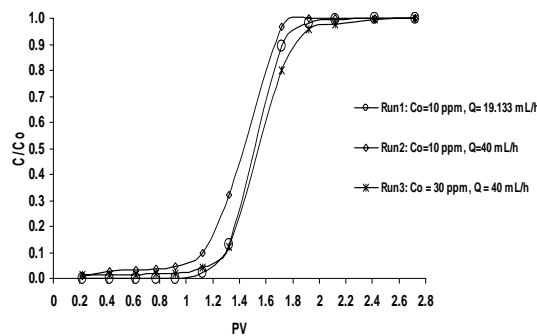


Figure 2.5 Breakthrough curves of Cr(VI) through Liwa soil.

There are little deviations in the shape of BTCs suggesting that differences in the initial concentration used or differences between the two flow rates employed do not result in a significant impact on the shape of BTC. Furthermore, Cr behavior was as expected with little shift to the right from an ideal tracer, indicating that Cr is encountering little sorption during transport through the column. The transport parameters D and R were determined by curve fitting using CXTFIT2 model as presented below.

3.0 Results and Discussion

3.1 Results of the miscible displacement experiments

Normalized effluent Cr(VI) concentration along with the corresponding values of the pore volume (PV) were utilized to determine the value of D and R . The equilibrium advection-dispersion model that accounts for sorption (Mode 1 of CXTFIT) has been used for this purpose. The value of pore water velocity was determined independently from the value of flow rate, moisture content and cross-sectional area of the column ($v_o = Q/\theta A$) and the degradation rate was set to zero. Both D and R were set as unknowns. Model outputs are presented in Table 5.1.

Table 1 Values of R and D as determined by the CXTFIT.

Co, ppm	v _o , cm/hr	D, cm ² /hr	R	r ²	D/v _o , cm	K _d , L/kg
10	2.866	0.93	1.51	1.000	0.324	0.090
10	5.992	2.72	1.41	0.996	0.454	0.072
30	5.992	2.75	1.55	0.999	0.459	0.097
Average			1.49		0.412	0.086

Table 1 shows that the dispersion coefficient increases as the pore-water velocity increases. This behavior is well documented in the literature. The ratio D/v_o is denoted as dispersivity which is a characteristic of the porous media. The value of dispersivity is expected to be constant regardless of the flow rate. The values of dispersivity in this study ranges between 0.324-0.459 cm with an average value of 0.41 cm.

Table 4.5 shows that the retardation factor for the three runs ranges between 1.41-1.55 with an average value of 1.49. There was no trend of increase or decrease in R with changes in C_o or v_o. This is expected since the retardation factor is a function of both the chemical and the porous media. The value of R does not deviate much from 1.0 (ideal tracer), indicating that little sorption has occurred during Cr(VI) transport.

3.2 Treatment of Water for Chromium Removal

The main objectives of the treatment experiments were (1) to investigate the role of iron in reducing Cr(VI) to Cr(III), and (2) to investigate the role of granular activated carbon (GAC) in sorbing chromium.

3.3 Reduction of Cr(VI) using iron powder

Variations of Cr(VI) with time at pH 4 and 7 in the presence of iron are shown in Fig. 3.1. The figure shows a reduction in Cr(VI) concentration with time at both pH values. The rate of change of Cr(VI) concentration is high at initial times. The figure also shows that as the pH is reduced from 7 to 4 higher changes occurs with almost complete disappearance of Cr(VI) from solution at pH 4 after 2 hrs of contact time.

Figure 3.1 also shows variations in the total Cr in the aqueous solution as analyzed by the ICP. When the total Cr is higher than Cr(VI) it indicates that part of the reduced Cr(VI) is present in solution, possibly as Cr(III). Since, however, the total aqueous Cr does not correspond to the initial Cr(VI) concentration, it indicates that some of Cr(VI) is either being attached to the iron as Cr(VI) or is being reduced and attached to the iron.

Obviously, the addition of iron to the solution caused the disappearance of Cr(VI). At initial times, the reaction rate was very high but decreased until 6 hours. after 6 hrs we observed an increase in the concentration of Cr(VI) or total Cr in the solution followed by a decrease in concentration. This could be due to a high gradient created in the aqueous phase surrounding the iron particles, which later was stabilized as the reduction or sorption process reaches equilibrium.

As it is also clear, the concentration of total Cr after 6 hours is higher than Cr(VI). The difference should be a reduced form of Cr(VI), possibly Cr(III). Not all Cr(VI) disappeared from solution at pH 7. This appears to be in conflict with what has been reported by Hwang et al. who showed rapid and complete removal of Cr(VI) from solutions with a pH value of about 7.5 [2].

As the pH drops, we observed a decrease in the aqueous concentration of Cr(VI) and total Cr. Hwang et al. (2002) observed an increase in Cr removal with the increase in pH. The observed pH dependence in their work was explained on the basis that ferrous iron that makes a complex with Cr(III) which is preferable at higher values of pH since OH⁻ exists more. In our case, it is clear that most of the disappeared Cr(VI) is not in solution but adhered to the surface of the iron. The possibility that some of the disappeared Cr(VI) is precipitated as Cr(OH)₃ is low given that little OH⁻ exists in solution at pH 4.

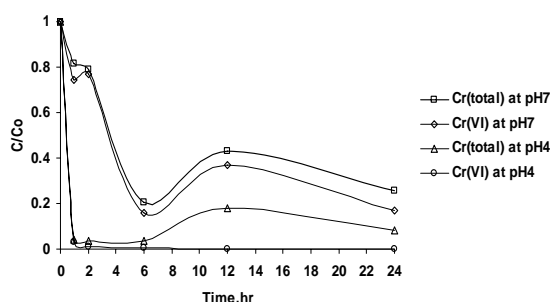


Figure 3.1 Variation of chromium concentration with time in the presence of iron at different values of pH. Initial Cr(VI) concentration = 10 ppm.

3.4 Removal of Chromium using granular activated carbon

Figure 3.2 shows the rate of change of Cr(VI) and total Cr concentration with the use of GAC at pH 9, 7 and 4. The concentration of Cr(VI) decreases with time in the presence of GAC, with more disappearance from solution as the pH drops. Results obtained by analyzing the samples using the ICP show a similar trend for total Cr. However, total Cr concentration is always higher than Cr(VI) concentration, indicating that some of Cr(VI) has been reduced to another chromium form and remains in solution. Figure 3.2 also demonstrates that the difference between Cr(VI) and total Cr concentration increases as the pH drops.

Hu et al. found that the uptake of Cr(VI) increases with increasing pH from 2 to 3 and then decreases from pH 3 to 6.5 [1]. This indicates that the solution pH affects the Cr(VI) adsorption. They concluded that an acidic solution at a pH value about 3 is an optimal condition for the adsorption of Cr(VI). This observation is consistent with what we found in our experiment.

Our experiment demonstrates that Cr(VI) can be removed from solution using GAC, but the mechanism of its removal is not solely sorption to carbon surface. It is possible that Cr(VI) is not being sorbed to the carbon surface but it is being reduced and the reduced form is being sorbed. Further experiments are needed to elucidate the exact mechanism(s) of Cr(VI) removal in the presence of activated carbon. The literature lacks results regarding this point. The reason why carbon reduces Cr(VI) also needs to be investigated.

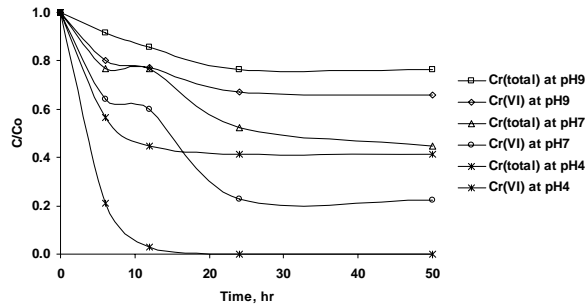


Figure 3.2 Variation of Cr concentration with time (mass of GAC = 0.5 g).

3.5 Chromium Sorption isotherm to GAC

Figures 3.3 and 3.4 show the sorption isotherm of Cr(VI) and Cr(III) using GAC, respectively. These experiments were conducted at pH 7 and a sampling time of 30 hrs. Such time is sufficient to reach equilibrium between the sorbed and the aqueous concentration (Figure 3.2). Comparison between Figures 3.3 and 3.4 shows that the capacity of GAC to sorb Cr(III) is higher than that when the solution contains initially Cr(VI). The sorption distribution coefficient, i.e. K_d for Cr(III) = 4.032 L/g while that for a solution containing initially Cr(VI) = 0.157 L/g.

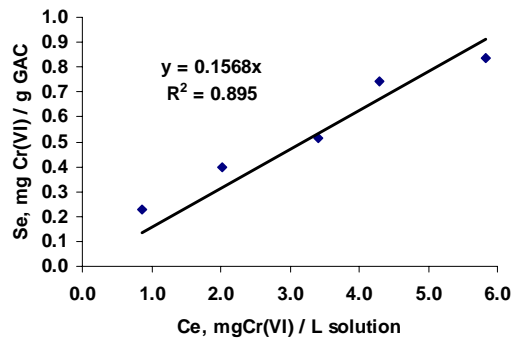


Figure 3.3 Sorption isotherm of Cr(VI) on GAC. S/W= 1/200.

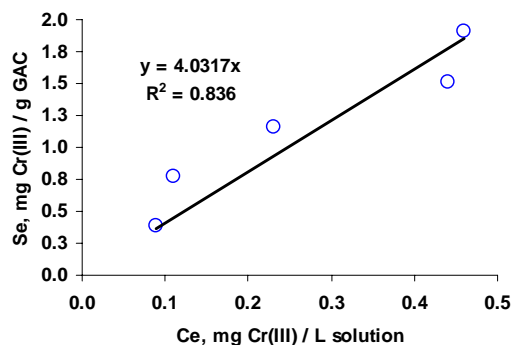


Figure 3.4 Sorption isotherm of Cr(III), S/W ratio= 1/200.

4.0 Conclusion

The main objectives of this study were to investigate the predominant mechanisms affecting the transport of Cr(VI) through columns packed with Liwa soil material and to investigate the

efficiency of activated carbon and iron in removing Cr(VI) from groundwater. Based on this study the following conclusions can be made:

1. The concentration of total chromium in groundwater at Liwa area slightly exceeds the MCL, but the concentration of Cr(VI) exceeds the MCL for drinking water by two folds.
2. Batch rate experiments using soil material from Liwa area revealed that the capacity of soil to sorb Cr(VI) is negligible, but the capacity to sorb Cr(III) is relatively high. This behavior was attributed to the affinity of Cr(III) to adhere to the negatively charged silt particles.
3. Batch sorption isotherm of Cr(VI) showed a low distribution coefficient of 0.03 L/kg, but the column transport study resulted in a three times higher value. The lower value of K_d found from the batch experiment could be due to the inability to accurately determine the value with a low S/W ratio when the chemical is not being greatly sorbed to the soil.
4. Results of the conducted miscible displacement experiments suggested that differences in the initial concentration used or differences among the flow rates employed do not result in a significant impact on the shape of the BTCs for Cr(VI).
5. The dispersivity of columns packed with soil material from Liwa area averages 0.4 cm.
6. Batch rate study for removal of Cr(VI) from aqueous solution using iron showed high removal rate at initial times.
7. Removal of Cr(VI) from aqueous solution using iron appears to increase as the pH drops with almost complete disappearance of Cr(VI) at pH 4.
8. After treatment with iron, the total Cr in aqueous solution was higher than Cr(VI) but lower than the initial Cr(VI) concentration, suggesting that some of Cr(VI) either being attached to the iron as Cr(VI) or is being reduced and then attached to the iron.
9. Treatment of aqueous solution containing Cr(VI) with activated carbon resulted in higher removal of Cr(VI) from solution as the pH dropped.
10. The mechanism of Cr(VI) removal by GAC was not solely sorption to carbon surface since the total Cr in solution, after treatment, was higher than Cr(VI) but lower than the initial Cr(VI) concentration. It is speculated that Cr(VI) reduced to Cr(III) and the reduced form was sorbed to the carbon surface.
11. The capacity of GAC to sorb Cr(III) is higher than that of Cr(VI).

References

- [1] Hu, Z., Lei, L., Li, Y., and Ni, Y., "Chromium adsorption on high-performance activated carbons from aqueous solution", *Separation and Purification Technology*, **31** (1), 13 – 18 (2003).
- [2] Hwang, I., Batchelor, B., Schlautman, M.A., and Wang, R., "Effects of ferrous iron and molecular oxygen on chromium (VI) redox kinetics in the presence of aquifer solids", *Journal of Hazardous Materials*, **92** (2), 143-159 (2002).